



ELSEVIER

Journal of Chromatography A, 850 (1999) 29–41

JOURNAL OF
CHROMATOGRAPHY A

Critical comparison of retention models for the optimisation of the separation of anions in ion chromatography

II. Suppressed anion chromatography using carbonate eluents

John E. Madden, Paul R. Haddad*

School of Chemistry, University of Tasmania, GPO Box 252-75, Hobart 7001, Tasmania, Australia

Abstract

Seven theoretical retention models, namely the linear solvent strength model (using the dominant equilibrium approach and competing ion effective charge approach), the dual eluent species model, the Kuwamoto model, the extended dual eluent species model, the multiple species eluent/analyte model and the empirical end-points model, were used to describe the retention behaviour of anions in suppressed ion chromatography (IC). An extensive set of experimental retention data was gathered for 24 anions (fluoride, formate, bromate, chloride, hexanesulfonate, bromide, chlorate, nitrate, iodide, thiocyanate, perchlorate, sulfite, succinate, sulfate, tartrate, selenate, oxalate, tungstate, phthalate, molybdate, chromate, thiosulfate and phosphate) on a Dionex AS4A-SC column using carbonate eluents of varying concentration and $\text{HCO}_3^-:\text{CO}_3^{2-}$ ratios. Statistical comparison of the predicted and experimentally obtained retention factors showed that the performance of the theoretical models improved with the complexity of the model. However the empirical model (in which a linear relationship is assumed between the logarithm of retention factor and the logarithm of eluent strength, but the slope is determined empirically) gave the most consistent performance across the widest range of anions. The empirical end-points model was also shown to be the most satisfactory model due to its low knowledge requirements and easy solution. Compared with non-suppressed IC (see Part I), the retention behaviour in suppressed IC was found to be easier to model by all retention models. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Retention models; Optimisation; Inorganic anions

1. Introduction

A computer-assisted interpretive optimisation procedure requires a retention model providing a mathematical relationship for calculation of the retention factor of an analyte under differing eluent conditions. The first step in the development of a computer-based interpretive optimisation method is the selection of a suitable retention model so that retention factors (k') can be predicted under a range of eluent

conditions. In a previous paper [1], we have evaluated seven retention models for their accuracy, precision and ease of solution for the prediction of analyte retention factors under a range of stationary phase and mobile phase conditions used in non-suppressed ion chromatography (IC). This work concentrated solely on phthalate eluents used at acidic pH values, so that at most, the eluent contained two competing ions (phthalate and hydrogen phthalate). In that study we showed that none of the theoretical models was sufficiently rugged to permit reliable prediction of retention factors, but that the retention data showed good linearity for a plot of log

*Corresponding author. Fax: +61-3-6226-2858.

E-mail address: paul.haddad@utas.edu.au (P.R. Haddad)

k' versus $\log [\text{eluent}]$, even when there were two competing ions present in the eluent. However, the slope of this relationship could not be predicted reliably from theory. In view of this, we have proposed that the best prediction of retention factors using minimal experimentation can be achieved by measuring retention factors for each analyte at several extremes of eluent composition (i.e., extremes of pH and concentration) and then interpolating retention factors at intermediate compositions by assuming a linear relationship between $\log k'$ and $\log [\text{eluent}]$. This approach was referred to as an “empirical end-points model”.

We turn now to an evaluation of the same models for use in suppressed IC using carbonate/hydrogencarbonate mixtures as eluents. Such re-evaluation is necessary both because of the different natures of the stationary and mobile phases in comparison to non-suppressed IC and also because the suppressed IC eluents are used at high pH, so the hydroxide ion must be considered as a third competing anion in addition to carbonate and hydrogencarbonate.

2. Theory

The models to be compared have been discussed in full mathematical detail in the previous article [1] and this information will not be repeated here. However, a brief description of each model will be presented here with further discussion added when the higher pH eluents used in suppressed IC can exert an influence on the model.

2.1. Linear solvent strength models

The linear solvent strength models [2–4] are based on a linear relationship between $\log k'$ and $\log [\text{eluent}]$, but when the eluent contains more than one competing ion, two approaches emerge, namely the dominant equilibrium approach and the effective charge approach [5]. The dominant equilibrium approach is the simplest of the multiple species retention models and assumes that only the most highly charged species is responsible for elution, simplifying the system to a single species retention mechanism. That is, only the effect of carbonate needs to be considered under this approach when

suppressed IC eluents are used. The effective charge approach considers that all eluent species participate in elution and the strength of each species is directly proportional to its charge.

2.2. Dual eluent species model

The dual eluent species model [6–8] is a simplification of the Hoover model [1,9] in that it assumes no elution from hydroxide on the basis that concentrations are usually very low in most eluents and hydroxide is a very weak competing ion in anion-exchange systems. This assumption was valid for non-suppressed IC systems but may not be appropriate for the high pH values used in suppressed IC.

2.3. Kuwamoto model

The Kuwamoto model [10] is a further simplification of the Hoover model but replaces ion-exchange selectivity constants with elution system coefficients. These coefficients have less physical meaning than ion-exchange selectivity constants, but serve to simplify the solution of the model in practical examples.

2.4. Extended dual eluent species model

The extended dual eluent species model [11] is an amplification of the dual eluent species model. The same assumptions are made, but an added empirical term is introduced to improve the performance of the model for species (both eluents and analytes) whose charge changes as pH is altered.

2.5. Multiple species eluent/analyte model

The multiple species eluent/analyte model [12] model includes all of the interactions of multiple analyte and eluent species, and also accounts for changes in speciation with pH. When applied to non-suppressed IC, this model did not consider the contribution from hydroxide because of the low eluent pH values used. However, the influence of hydroxide will need to be included when the model is applied to suppressed IC.

2.6. Empirical end-points model

As discussed earlier, the empirical end-points model [1] was derived from the linear solvent strength model, but modified to allow purely empirical measurement of the slope rather than to rely on the theoretically derived value.

3. Experimental

3.1. Retention data

Statistical analyses of the performance of the various retention models were carried out using experimental retention data acquired using the IC system described below. All calculations were performed using Microsoft Excel 97 on a Pentium MMX 200 computer with 64 MB of SDRAM, running Windows NT workstation v4.0 sp3.

3.1.1. Reagents and solutions

Eluents were prepared by using analytical grade NaHCO_3 (May and Baker, West Footscray, Australia) and Na_2CO_3 (Ajax, Auburn, Australia). Ultra-pure water was purified using a Milli-Q system (Millipore, Bedford, MA, USA) containing a 0.45- μm filter at the outlet. Sample solutions of fluoride, formate, bromate, chloride, nitrite, hexanesulfonate, bromide, chlorate, nitrate, phosphate, sulfite, succinate, sulfate, tartrate, selenate, oxalate, iodide, tungstate, phthalate, molybdate, chromate, thiosulfate, thiocyanate and perchlorate were prepared by dissolution of analytical grade salts in the sodium form (formate, nitrate, chromate, chloride, perchlorate, bromate, phthalate, nitrite and selenate from Ajax, iodide, chlorate, phosphate, thiosulfate and tungstate from BDH Chemicals, Kilsyth, Australia, tartrate and oxalate from Mallinckrodt, Paris, KY, USA, fluoride and sulfate from Prolabo, Paris, France, bromide and hexanesulfonate from Sigma, St. Louis, MO, USA, thiocyanate and succinate from Aldrich, Milwaukee, WI, USA and sulfite from Chem-Supply, Beverley, Australia). The concentrations of the anions varied from 2 mg/l to 200 mg/l. The samples were analysed at five eluent concentrations ($[\text{HCO}_3^{2-}] + [\text{CO}_3^{2-}] = 2, 3, 4, 5$ and 6 mM) and seven carbonate-to-hydrogencarbonate ratios ($\% \text{ CO}_3^{2-} = 10, 20, 40,$

50, 60, 80 and 90%), i.e., at 35 different eluent compositions.

3.1.2. Instrumentation

The chromatographic instrumentation consisted of a Dionex DX-500 ion chromatograph (Dionex, Sunnyvale, CA, USA), a Dionex AS4A-SC anion separator column ($250 \times 4 \text{ mm}$), and a Dionex ASRS-1 self-regenerating suppressor housed in an LC30 chromatography oven, a Dionex ED40 electrochemical detector operated in the conductivity mode and a GP40 gradient pump in the isocratic mode. The injection loop was $25 \mu\text{l}$. All samples were analysed in duplicate with a flow-rate of 2.0 ml/min .

3.2. Methods for solution of models

In this section, specific experimental procedures for solving each of the models are presented. Details of the mathematical symbols used in each model may be found in our previous publication in this series [1].

3.2.1. Linear solvent strength model; dominant equilibrium approach

Only one experimental data point was required to solve for the parameter C_1 in this model, which could be calculated by rearranging the linear solvent strength model. Values for k'_A and $[\text{E}^{2-}]$ were obtained from the total eluent concentration of 2 mM and $\% \text{ CO}_3^{2-} = 10\%$, see Table 1.

3.2.2. Linear solvent strength model; effective charge approach

The following equations were used to calculate C_1 and C_2 :

$$C_2 = \left[\log \left(\frac{k'_{A1}}{k'_{A2}} \right) + \left(\frac{x}{y_{\text{eff1}}} - \frac{x}{y_{\text{eff2}}} \right) \log (E_T) \right] / \log \left(\frac{y_{\text{eff2}}}{y_{\text{eff1}}} \right) \quad (1)$$

$$C_1 = \log k'_{A1} - C_2 \log \left(\frac{1}{y_{\text{eff1}}} \right) + \frac{x}{y_{\text{eff1}}} \log (E_T) \quad (2)$$

Table 1
Experimental data points used to solve each retention model

Model	Experiment No.	[Eluent] (mM)	% CO_3^{2-}
Dominant equilibrium approach	1	2.0	10
Effective charge approach	1	2.0	10
	2	2.0	90
Dual eluent species	1	2.0	10
	2	6.0	90
Kuwamoto	1	2.0	10
	2	2.0	90
Extended dual eluent species	1	2.0	10
	2	6.0	10
	3	2.0	90
Multiple species eluent/analyte (singly or doubly charged)	1	2.0	10
	2	2.0	50
	3	2.0	90
Multiple species eluent/analyte (partially doubly or partially triply charged)	1	2.0	10
	2	2.0	40
	3	2.0	60
	4	2.0	90
Empirical end-points	1	2.0	10
	2	2.0	90
	3	6.0	10
	4	6.0	90

where y_{eff} is the effective charge of the eluent species and E_T is the total eluent concentration.

Values for k'_A and $[E_T]$ were obtained from the experimental data with a total eluent concentration of 2.0 mM and % CO_3^{2-} = 10% and 90%, see Table 1.

3.2.3. Dual eluent species model

Two experimental data points were required to determine the ion-exchange selectivity constants for this model. These experiments could be any combination of total eluent concentration or pH, but it is desirable that the two data points used should have the maximum and minimum values for eluent concentration and pH. $K_{A,HE}$ was determined by rearranging the dual eluent species model and solving for k'_A using an arbitrary value of $K_{E,HE}$. $K_{E,HE}$ was then solved numerically by altering its value until the value for k'_A matched the second experimentally determined value. Choice of the arbitrary value of

$K_{E,HE}$ was found to be critical in order to find a solution.

Values for k'_A and $[E_T]$ were obtained from the experimental data using a total eluent concentration of 2.0 mM containing 10% CO_3^{2-} , and a total eluent concentration of 6.0 mM containing 90% CO_3^{2-} , see Table 1.

3.2.4. Kuwamoto model

Two experimental data points were required to determine the elution system coefficients. For the first data point a low pH was necessary to ensure that elution due to the divalent species can be neglected. The elution system coefficients were calculated using the following equations:

$$C_2 = \frac{1}{E_T} \left\{ \frac{(K_{a_2} + [\text{H}^+]_{m1})}{K_{a_2}} \right\} (k'_{A1})^{-2/x} \quad (3)$$

$$C_1 = \left(\frac{1}{E_T} - C_2 \left\{ \frac{K_{a_2}}{(K_{a_2} + [H^+]_{m2})} \right\} (k'_{A_2})^{2/x} \right) \times \left\{ \frac{(K_{a_2} + [H^+]_{m2})}{[H^+]_{m2}} \right\} (k'_{A_2})^{-1/x} \quad (4)$$

where C_1 and C_2 are elution system coefficients.

C_2 was calculated using values for k'_A and E_T taken from experiments where total eluent concentration was 2.0 mM containing 10% CO_3^{2-} . C_1 was calculated using experimental data points obtained with a total eluent concentration of 2.0 mM and 90% CO_3^{2-} , see Table 1.

3.2.5. Extended dual eluent species model

This model simplifies to the dual eluent species model for the majority of analytes whose charge remains unchanged over the pH range of the eluent. For those analytes that did change their charge as the carbonate-to-hydrogencarbonate ratio was changed, the extended form of the model could be used.

First, the ion-exchange selectivity constant and the empirical relationship $\{10^{[a(e)+b]}\}$ were determined using two experiments of identical pH. This ensured that e remained constant so the empirical relationship would also remain constant. The solution was achieved in a similar way to the dual eluent species model, however the empirical relationship, $\{10^{[a(e)+b]}\}$ was solved by rearrangement of the extended dual eluent species model while $K_{E,HE}$ was determined using the iterative process described for the dual eluent species model.

To solve for the empirical constants, a and b , a third experiment was used having an identical eluent concentration to the first experiment, but a different carbonate-to-hydrogencarbonate ratio. This ensured that both $\{10^{[a(e)+b]}\}$ and e change. Thus a and b could be calculated using the following equations:

$$a = \log \left[\frac{\{10^{[a(e)+b]}\}_1}{\{10^{[a(e)+b]}\}_3} \right] / (e_1 - e_3) \quad (5)$$

$$b = \log \{10^{[a(e)+b]}\}_1 - a(e_1) \quad (6)$$

The selectivity constant and the empirical relationship were calculated using values for k'_A obtained from the experimental data with total eluent concentration of 2.0 and 6.0 mM, both containing 10%

CO_3^{2-} . To solve for the empirical constants a third value of k'_A was taken from the experimental data with total eluent concentration of 2.0 mM and 90% CO_3^{2-} , see Table 1.

3.2.6. Multiple species eluent/analyte model

Solutions for this model varied in complexity depending on the charge and speciation of the analyte. The methods used for solution of this model will be broken into four parts dealing with each of the four possibilities for this model. The fifth possibility, a triply charged anion, will not be covered as none of the anions fell into this category at the pH values studied here.

3.2.6.1. Singly or partially singly charged analyte anion

For this case the model simplifies to:

$$k'_A = \frac{wK_{A,HE}}{V_m} \left(\frac{\sqrt{p^2 + 8K_{E,HE}Q[E^{2-}] - p}}{4K_{E,HE}[E^{2-}]_m} \right) \frac{[A^-]_m}{A_T} \quad (7)$$

where $p = [HE^-] + K_{OH,HE}[OH^-]$ and A^{x-} is the analyte species and A_T is the total concentration of the analyte.

Three experimental data points are required to solve this model. $K_{A,HE}$ can be determined using the following equation:

$$K_{A,HE} = \frac{k'_{A1}V_m}{w} \left(\frac{4K_{E,HE}[E^{2-}]_{m1}}{\sqrt{p_1^2 + 8K_{E,HE}Q[E^{2-}]_{m1} - p_1}} \right) \frac{A_T}{[A^-]_{m1}} \quad (8)$$

The remaining two ion-exchange selectivity constants, $K_{P,HP}$ and $K_{OH,HP}$ must be calculated using an iterative process.

The ion-exchange selectivity constants were calculated using values of k'_A , $[HE^-]$, $[E^{2-}]$ and $[A^-]/A_T$ obtained from the experimental data points with a total eluent concentration of 2.0 mM and % CO_3^{2-} of 10%, 50% and 90%, see Table 1.

3.2.6.2. Doubly charged analyte anion

For this case the model simplifies to:

$$k'_A = \frac{wK_{A,HE}}{V_m} \left(\frac{\sqrt{p^2 + 8K_{E,HE}Q[E^{2-}]_m} - p}{4K_{E,HE}[E^{2-}]_m} \right)^2 \quad (9)$$

Three experiments were required to obtain a solution using an identical process to that employed for the singly or partially singly charged anion, but using the following equation to solve for $K_{A,HE}$:

$$K_{A,HE} = \frac{k'_{A1}V_m}{w} \left(\frac{4K_{E,HE}[E^{2-}]_{m1}}{\sqrt{p_1^2 + 8K_{E,HE}Q[E^{2-}]_{m1}} - p_1} \right)^2 \quad (10)$$

3.2.6.3. Partially doubly charged analyte anion

For this case the model simplifies to:

$$\begin{aligned} k'_A &= \frac{wK_{A,HE}}{V_m} \left(\frac{\sqrt{p^2 + 8K_{E,HE}Q[E^{2-}]_m} - p}{4K_{E,HE}[E^{2-}]_m} \right) \frac{[A^{2-}]_m}{A_T} \\ &+ \frac{wK_{HA,HE}}{V_m} \left(\frac{\sqrt{p^2 + 8K_{E,HE}Q[E^{2-}]_m} - p}{4K_{E,HE}[E^{2-}]_m} \right) \frac{[HA^-]_m}{A_T} \end{aligned} \quad (11)$$

A total of four experiments were required to solve for the ion-exchange selectivity constants. Two initial experiments and the following equations are used to solve for $K_{A,HP}$ and $K_{HA,HP}$:

$$\begin{aligned} K_{HA,HE} &= \frac{V_m}{w} \\ &\times \frac{\left[k'_{A1} - k'_{A2} \frac{\text{factor}_1^2 [A^{2-}]_{m1}}{\text{factor}_2^2} \frac{A_T}{[A^{2-}]_{m2}} \right]}{\left[\frac{\text{factor}_1^2 [HA^-]_{m1}}{A_T} - \frac{\text{factor}_2^2 [HA^-]_{m2}}{A_T} \frac{\text{factor}_1^2 [A^{2-}]_{m1}}{\text{factor}_2^2} \frac{A_T}{[A^{2-}]_{m2}} \right]} \end{aligned} \quad (12)$$

$$\begin{aligned} K_{A,HE} &= \frac{V_m}{w} \left[k'_{A1} - \frac{wK_{HA,HE}}{V_m} \text{factor}_1 \frac{[HA^-]_{m2}}{A_T} \right] \\ &\times \frac{1}{\text{factor}_1^2} \frac{A_T}{[A^{2-}]_{m1}} \end{aligned} \quad (13)$$

where

$$\text{factor}_n = \left(\frac{\sqrt{p_n^2 + 8K_{E,HE}Q[E^{2-}]_{mn}} - p_n}{4K_{E,HE}[E^{2-}]_{mn}} \right)$$

A third and fourth experiment were then used to solve for $K_{E,HE}$ and $K_{OH,HE}$ by an iterative minimisation process.

The ion-exchange selectivity constants, $K_{A,HE}$ and $K_{HA,HE}$ were calculated using values of k'_A , $[HE^-]$, $[E^{2-}]$, $[HA^-]/A_T$ and $[A^{2-}]/A_T$ obtained from the experimental data points with total eluent concentration of 2.0 mM and % CO_3^{2-} of 10 and 90%. $K_{E,HE}$ and $K_{OH,HE}$ were then calculated from a third and fourth experiment using values of k'_A , $[HE^-]$, $[E^{2-}]$, $[HA^-]/A_T$ and $[A^{2-}]/A_T$ obtained from the experimental data points with total eluent concentration of 2.0 mM and % CO_3^{2-} of 40 and 60%, see Table 1.

3.2.6.4. Partially triply charged analyte anion

For this case the model simplifies to:

$$\begin{aligned} k'_A &= \frac{wK_{A,HE}}{V_m} \left(\frac{\sqrt{p^2 + 8K_{E,HE}Q[E^{2-}]_m} - p}{4K_{E,HE}[E^{2-}]_m} \right)^3 \frac{[A^{3-}]_m}{A_T} \\ &+ \frac{wK_{HA,HE}}{V_m} \left(\frac{\sqrt{p^2 + 8K_{E,HE}Q[E^{2-}]_m} - p}{4K_{E,HE}[E^{2-}]_m} \right)^2 \frac{[HA^{2-}]_m}{A_T} \end{aligned} \quad (14)$$

Four experiments were required to solve this model. The entire process for solution is identical to that used for the partially doubly charged anion, but using the following equations to solve for $K_{A,HE}$ and $K_{HA,HE}$:

$$\begin{aligned} K_{HA,HE} &= \frac{V_m}{w} \\ &\times \frac{\left[k'_{A1} - k'_{A2} \frac{\text{factor}_1^3 [A^{3-}]_{m1}}{\text{factor}_2^3} \frac{A_T}{[A^{3-}]_{m2}} \right]}{\left[\frac{\text{factor}_1^2 [HA^{2-}]_{m1}}{A_T} - \frac{\text{factor}_2^2 [HA^{2-}]_{m2}}{A_T} \frac{\text{factor}_1^3 [A^{3-}]_{m1}}{\text{factor}_2^3} \frac{A_T}{[A^{3-}]_{m2}} \right]} \end{aligned} \quad (15)$$

$$\begin{aligned} K_{A,HE} &= \frac{V_m}{w} \left[k'_{A1} - \frac{wK_{HA,HE}}{V_m} \text{factor}_1^2 \frac{[HA^{2-}]_{m1}}{A_T} \right] \\ &\times \frac{1}{\text{factor}_1^3} \frac{A_T}{[A^{3-}]_{m1}} \end{aligned} \quad (16)$$

where

$$\text{factor}_n = \left(\frac{\sqrt{p_n^2 + 8K_{\text{E,HE}}Q[\text{E}^{2-}]_{mn}} - p_n}{4K_{\text{E,HE}}[\text{E}^{2-}]_{mn}} \right)$$

3.2.7. Empirical end-points model

Four experimental data points were required to solve this model. As the name suggests, these four data points must lie at the four extreme points of the desired search area of eluent compositions, defined by minimum and maximum eluent concentrations and carbonate-to-hydrogencarbonate ratios.

The values for the four chromatographic constants f_{1-4} can be solved using the following equations:

$$\begin{aligned} f_2 &= \frac{(C_{11} - C_{12})}{(E_{T1} - E_{T2})}; \\ f_1 &= C_{11} - f_2 E_{T1}; \\ f_4 &= \frac{(C_{21} - C_{22})}{(E_{T1} - E_{T2})}; \\ f_3 &= C_{21} - f_4 E_{T2} \end{aligned} \quad (17)$$

where

$$\begin{aligned} C_{21} &= \log \left(\frac{k'_{A1}}{k'_{A2}} \right) / \log \left(\frac{[\text{CO}_3^{2-}]_{m1}}{[\text{CO}_3^{2-}]_{m2}} \right); \\ C_{11} &= \log(k'_{A1}) - C_{21} \log[\text{CO}_3^{2-}]_{m1}; \\ C_{22} &= \log \left(\frac{k'_{A3}}{k'_{A4}} \right) / \log \left(\frac{[\text{CO}_3^{2-}]_{m3}}{[\text{CO}_3^{2-}]_{m4}} \right); \\ C_{12} &= \log(k'_{A3}) - C_{22} \log[\text{CO}_3^{2-}]_{m3} \end{aligned} \quad (18)$$

The chromatographic constants were calculated using values for k'_A obtained from the experimental data with total eluent concentration of 2.0 and 6.0 mM, and % CO_3^{2-} of 10 and 90%, see Table 1.

4. Results and discussion

4.1. Prediction of retention times using the models

Once the various parameters for each model had been found, the models were used to predict retention data for all 24 analytes using each of the eluent compositions in the data set. This gave a total of $24 \times 35 = 840$ predicted retention times for each

model. Table 2 shows a typical set of results for sulfate. The measured retention times are shown for each eluent composition, as well as those predicted by each of the seven models.

From these data the normalised percentage difference (% d_i) between the measured and predicted retention times for a particular ion (i) was calculated using the following equation:

$$\% d_i = \frac{t_{R \text{ act}} - t_{R \text{ pred}}}{t_{R \text{ act}} + t_{R \text{ pred}}} \cdot 2 \cdot \frac{100}{1} \quad (19)$$

where $t_{R \text{ act}}$ is the experimentally determined retention time and $t_{R \text{ pred}}$ is the retention time predicted by the model.

Table 3 shows the values of % d_i for the data given in Table 2, i.e., for the retention of sulfate. If a model represents the data adequately, the normalised percentage differences should possess characteristics that do not refute the basic assumption that the differences are randomly distributed about the $t_{R \text{ pred}}$ values, i.e., that they have a Gaussian distribution. Systematic departures from randomness indicate that the model is not satisfactory. A study of the signs and magnitude of the normalised percentage differences can aid further in the analysis of the data.

If the values of % d_i are now averaged for a particular ion (to give % d_{av}), graphical representations of the performance for each model can be obtained, as shown in Fig. 1.

4.2. Overall results for all analytes

Data similar to Tables 2 and 3 could be generated for each of the 24 analytes, however the volume of data necessitates the use of a statistical approach in order that trends may be identified. The statistical operations carried out on these data are the same as those carried out for the non-suppressed data [1] in order that a direct comparison can be made.

The accuracy of the models for all analytes using various carbonate concentrations and carbonate-to-hydrogencarbonate ratios in the eluent can be assessed by the global average of the percentage normalised differences (% d_{glob}), which should be zero, i.e., a Gaussian distribution. The precision for each model at various carbonate concentrations and carbonate-to-hydrogencarbonate ratios for all ana-

Table 2

Experimentally measured retention times (E) and predicted retention times for sulfate using the seven retention models: dominant equilibrium approach (DE), effective charge approach (EC), dual eluent species model (DES), Kuwamoto model (K), extended dual eluent species model (ED), multiple species eluent/analyte model (MSE) and empirical end-points model (EEP)^a

Eluent composition		Retention time (min)							
% CO ₃ ²⁻	E _T	E	DE	EC	DES	K	ED	MSE	EEP
10	2.00	41.98	41.98	41.98	41.98	41.98	41.98	41.98	41.98
	3.00	26.66	28.26	20.73	27.16	26.53	27.17	26.06	27.68
	4.00	19.14	21.40	12.71	19.91	19.07	19.92	18.47	20.25
	5.00	15.87	17.28	8.79	15.64	14.74	15.65	14.10	15.69
	6.00	12.62	14.53	6.56	12.84	11.93	12.84	11.29	12.62
20	2.00	26.87	21.79	25.52	23.27	24.24	23.28	24.96	23.91
	3.00	16.62	14.79	13.59	15.41	15.81	15.41	16.09	15.92
	4.00	12.27	11.30	8.82	11.53	11.68	11.53	11.78	11.77
	5.00	9.82	9.20	6.38	9.22	9.24	9.23	9.25	9.22
	6.00	8.17	7.80	4.95	7.70	7.65	7.71	7.60	7.50
40	2.00	14.72	11.70	13.84	13.12	14.09	13.12	14.80	13.98
	3.00	9.63	8.07	8.24	8.91	9.48	8.91	9.90	9.45
	4.00	7.24	6.25	5.80	6.82	7.19	6.82	7.47	7.08
	5.00	5.83	5.17	4.47	5.57	5.84	5.57	6.03	5.63
	6.00	4.93	4.44	3.66	4.74	4.94	4.74	5.09	4.66
50	2.00	12.55	9.68	11.46	11.00	11.90	11.00	12.55	11.86
	3.00	8.17	6.72	7.11	7.53	8.09	7.53	8.49	8.06
	4.00	6.14	5.25	5.15	5.81	6.20	5.81	6.48	6.08
	5.00	5.02	4.36	4.06	4.78	5.07	4.78	5.28	4.87
	6.00	4.18	3.77	3.38	4.10	4.32	4.10	4.49	4.05
60	2.00	10.73	8.37	9.97	9.56	10.41	9.56	10.98	10.41
	3.00	7.03	5.83	6.40	6.60	7.13	6.60	7.51	7.11
	4.00	5.36	4.57	4.75	5.13	5.51	5.13	5.78	5.39
	5.00	4.32	3.82	3.81	4.25	4.54	4.25	4.75	4.34
	6.00	3.71	3.32	3.22	3.67	3.89	3.66	4.06	3.63
80	2.00	8.63	6.66	8.35	7.73	8.48	7.73	8.85	8.54
	3.00	5.72	4.71	5.65	5.41	5.90	5.41	6.17	5.89
	4.00	4.35	3.73	4.34	4.25	4.61	4.25	4.83	4.51
	5.00	3.61	3.15	3.58	3.56	3.84	3.56	4.02	3.66
	6.00	3.11	2.76	3.08	3.09	3.33	3.09	3.48	3.09
90	2.00	7.90	6.10	7.90	7.11	7.83	7.11	7.90	7.90
	3.00	5.29	4.33	5.45	5.00	5.48	5.00	5.59	5.47
	4.00	4.07	3.45	4.25	3.95	4.31	3.95	4.42	4.20
	5.00	3.37	2.92	3.53	3.32	3.60	3.32	3.70	3.43
	6.00	2.90	2.57	3.06	2.90	3.13	2.90	3.23	2.90

^a Carbonate eluents with a total concentration of E_T and carbonate-to-hydrogencarbonate ratio given as % CO₃²⁻ were used.

lytes is given by the standard deviation of the percentage normalised differences [$s_{d(\% d)}$], which should be zero. From the same data the correlation coefficient can also be calculated, which should be unity.

Data for % d_{glob} , $s_d(\% d)$ and the correlation coefficient for each model are given in Table 4. The data are presented in three ways that reflect the three different approaches to the optimisation of eluent composition in IC. In the first, the experimental and

Table 3

Normalised percentage differences (% d_i) between the measured and predicted retention times from the seven retention models: dominant equilibrium approach (DE), effective charge approach (EC), dual eluent species model (DES), Kuwamoto model (K), extended dual eluent species model (ED), multiple species eluent/analyte model (MSE) and empirical end-points model (EEP) for sulfate

Eluent composition		Normalised % difference (% d_i)						
% CO_3^{2-}	E_T	DE	EC	DES	K	ED	MSE	EEP
10	2.00	0	0	0	0	0	0	0
	3.00	−5.82	25.05	−1.87	0.51	−1.89	2.29	−3.77
	4.00	−11.13	40.41	−3.94	0.37	−3.99	3.59	−5.64
	5.00	−8.50	57.45	1.48	7.42	1.42	11.83	1.12
	6.00	−14.09	63.13	−1.69	5.67	−1.76	11.11	0
20	2.00	20.90	5.15	14.35	10.29	14.33	7.37	11.65
	3.00	11.62	20.04	7.56	5.03	7.53	3.23	4.29
	4.00	8.25	32.74	6.24	4.96	6.20	4.11	4.18
	5.00	6.51	42.44	6.26	6.05	6.21	5.99	6.33
	6.00	4.61	49.04	5.88	6.59	5.82	7.22	8.60
40	2.00	22.88	6.17	11.50	4.39	11.49	−0.55	5.16
	3.00	17.64	15.54	7.79	1.63	7.77	−2.71	1.94
	4.00	14.61	22.10	6.03	0.66	6.01	−3.16	2.18
	5.00	12.09	26.34	4.60	−0.10	4.57	−3.44	3.41
	6.00	10.47	29.68	3.93	−0.17	3.90	−3.10	5.73
50	2.00	25.81	9.07	13.21	5.31	13.21	0	5.66
	3.00	19.42	13.84	8.10	1.01	8.10	−3.88	1.37
	4.00	15.71	17.48	5.50	−0.91	5.49	−5.39	0.96
	5.00	14.11	21.06	4.85	−0.97	4.84	−5.07	3.12
	6.00	10.40	21.17	1.97	−3.33	1.95	−7.09	3.29
60	2.00	25.11	7.30	11.58	3.08	11.58	−2.33	3.05
	3.00	18.70	9.33	6.32	−1.46	6.32	−6.61	−1.14
	4.00	15.84	12.05	4.46	−2.71	4.46	−7.56	−0.63
	5.00	12.27	12.46	1.76	−4.88	1.75	−9.43	−0.43
	6.00	11.13	14.28	1.39	−4.77	1.38	−9.04	2.29
80	2.00	25.83	3.35	11.04	1.71	11.06	−2.55	1.06
	3.00	19.43	1.31	5.62	−3.11	5.63	−7.61	−2.89
	4.00	15.27	0.25	2.34	−5.86	2.35	−10.38	−3.55
	5.00	13.66	0.98	1.53	−6.20	1.53	−10.65	−1.35
	6.00	11.98	1.15	0.55	−6.76	0.55	−11.11	0.80
90	2.00	25.79	0	10.54	0.91	10.56	0	0
	3.00	19.87	−3.03	5.57	−3.50	5.58	−5.49	−3.34
	4.00	16.41	−4.28	2.96	−5.60	2.97	−8.13	−3.24
	5.00	14.16	−4.73	1.48	−6.63	1.49	−9.44	−1.65
	6.00	11.99	−5.41	0	−7.70	0	−10.67	0
Average (% d_{av})		12.37	16.08	4.83	0.03	4.81	−2.53	1.39

predicted data points used to assess the model are confined to those in which the carbonate content is 10% and the eluent concentration is varied. In the second approach the data points are those in which

the eluent concentration is kept constant at 2.0 mM and the carbonate-to-hydrogencarbonate ratio is varied. The third approach, labelled as two-dimensional, is where all the data points covering variations in

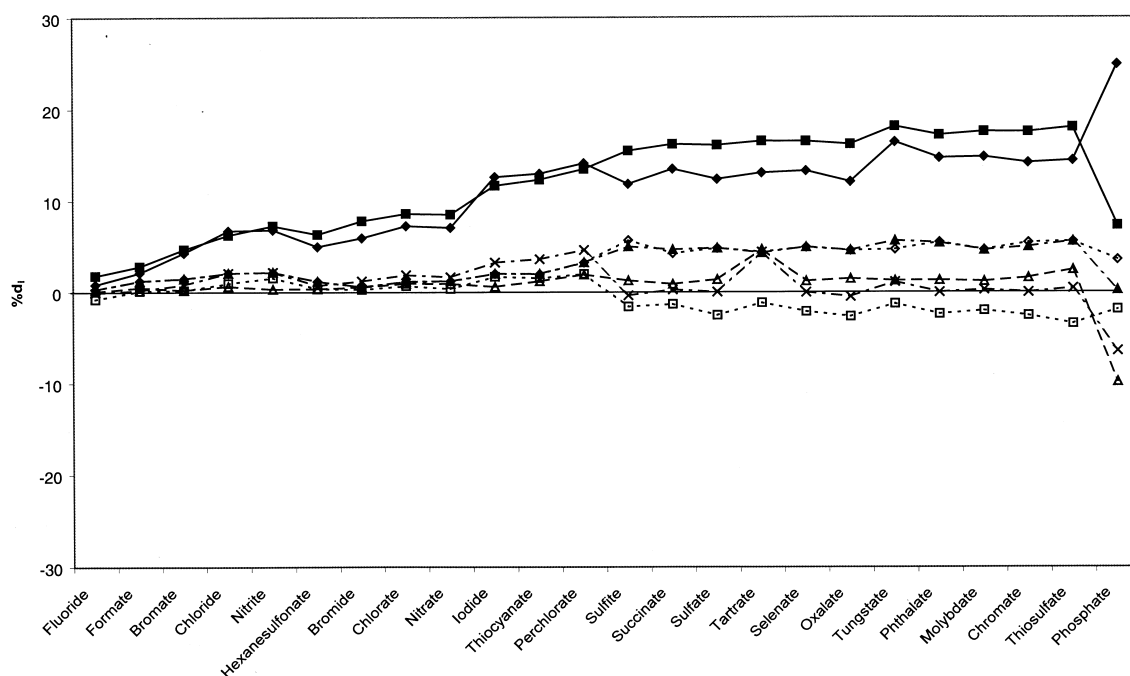


Fig. 1. Average of the normalised percentage differences between predicted and experimental data on the Dionex AS4A-SC column. \blacklozenge = Dominant equilibrium approach; \blacksquare = effective charge approach; \blacktriangle = dual eluent species model; \times = Kuwamoto model; \diamond = extended multiple eluent species model; \square = multiple species eluent/analyte model; \triangle = empirical end-points model.

both the eluent concentration and carbonate-to-hydrogencarbonate ratios are included. The success of each retention model in predicting retention times for each of these three scenarios can now be assessed.

The overall performance of each model can be best demonstrated using the correlation coefficient

between the predicted and experimental retention times. This is shown in Fig. 2 as a graph of the correlation coefficient for each analyte as well as the overall performance of each model for all analytes.

There are several other important factors that must be considered when comparing the utility and performance of the retention models and these factors

Table 4

Global average normalised percentage differences ($\% d_{\text{glob}}$) and correlation coefficients (Corr.) between the predicted and experimental data, and standard deviations of the percentage normalised differences ($s_d (\% d)$) for each retention model for three different types of optimisation technique (the best result in each category is shown in bold face)

Model	Constant carbonate-to-hydrogen-carbonate ratio			Constant total eluent concentration			Two-dimensional (overall)		
	$\% d_{\text{glob}}$	$s_d (\% d)$	Corr.	$\% d_{\text{glob}}$	$s_d (\% d)$	Corr.	$\% d_{\text{glob}}$	$s_d (\% d)$	Corr.
Dominant equilibrium approach	-5.16	5.02	0.99888	16.33	11.70	0.99361	10.89	10.33	0.99274
Effective charge approach	26.19	21.52	0.98204	3.19	3.12	0.99944	11.84	14.73	0.98816
Dual eluent species	1.51	4.28	0.99956	5.52	5.54	0.99815	3.07	4.22	0.99851
Kuwamoto	3.23	4.66	0.99960	2.57	3.64	0.99914	0.89	4.83	0.99919
Extended dual eluent	0.97	3.37	0.99960	5.84	5.66	0.99814	3.19	4.01	0.99842
Multiple species eluent/analyte	4.94	4.69	0.99918	0.53	2.37	0.99956	-0.67	5.22	0.99901
Empirical end-points	-1.22	2.22	0.99978	2.65	3.98	0.99892	0.72	4.03	0.99891

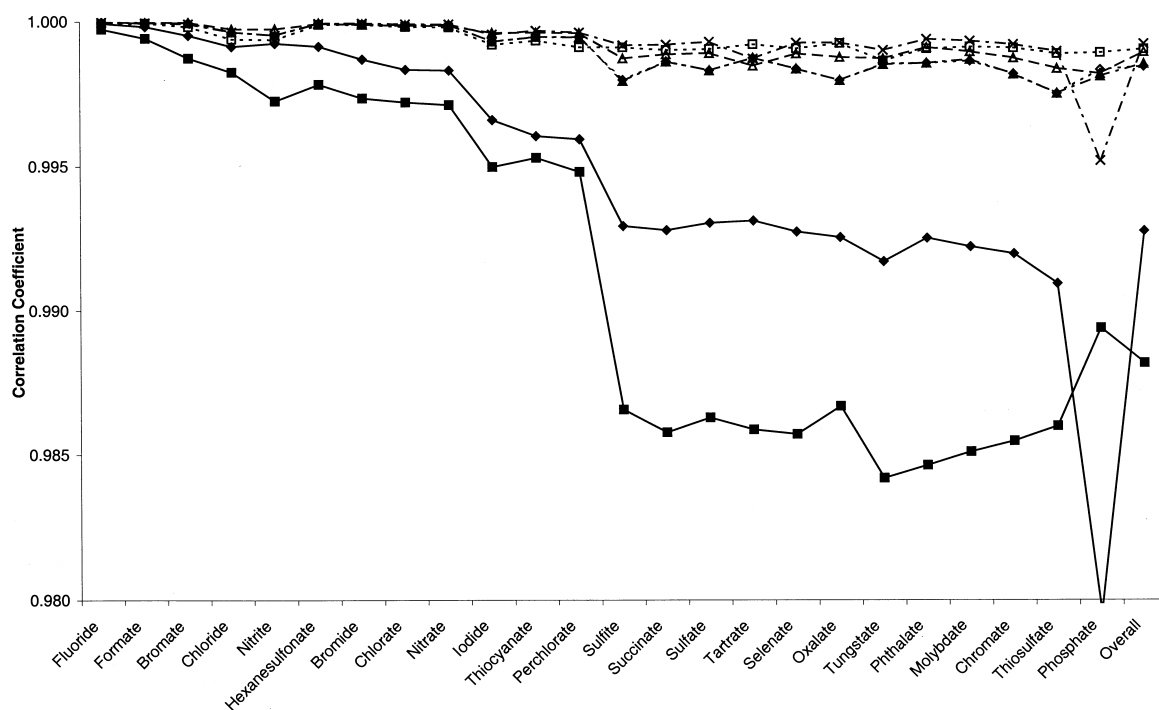


Fig. 2. Correlation coefficient between the predicted and experimental data for each individual analyte and overall on the Dionex AS4A-SC column. ♦=Dominant equilibrium approach; ■=effective charge approach; ▲=dual eluent species model; ×=Kuwamoto model; ◇=extended multiple eluent species model; □=multiple species eluent/analyte model; △=empirical end-points model.

are summarised in Table 5. The number of experiments required to solve the model should be as small as possible in order to maximise the speed of any optimisation routine using that model. In terms of the complexity of finding a solution, the models fall into two categories: those that have a linear solution and those that must be solved using a process of iterative

minimisation. Whilst the latter approach is more time consuming and demanding of computing power, all of the models proved to be relatively straightforward to solve, with the exception of the multiple species eluent/analyte model, which required the simultaneous determination of two or more non-linear constants. Furthermore, the choice of the starting

Table 5

Other important factors that must be considered when choosing a retention model for optimisation

Model	No. of experimental data points needed	Method used to solve model	Knowledge required to solve model
Dominant equilibrium approach	1	Linear solution	Analyte and eluent charge
Effective charge approach	2 (1) ^a	Linear solution	Analyte charge. pK_a of eluent
Dual eluent species	2	Iterative minimisation	Analyte charge. pK_a of eluent
Kuwamoto	2	Linear solution, but restricted pH selection	Analyte charge. pK_a of eluent
Extended dual eluent species	3 (2) ^b	Iterative minimisation	pK_a of eluent and analyte
Multiple species eluent/analyte	3 or 4	Iterative minimisation of two ion-exchange constants	pK_a of eluent and analyte
Empirical end-points	4 (2) ^a	Linear solution	pK_a of eluent

^a For one-dimensional experiment.

^b Simplifies to the dual eluent species model for some analytes.

point for the iterative minimisation process has a large influence on the chances of a solution being found, and the time taken to find a solution. This makes it difficult or impossible to completely automate the solution process. The amount of knowledge of the system required to find a solution is also a significant consideration. Most of the models require knowledge of the acid dissociation constant(s) of the eluent and some also require knowledge of the acid dissociation constant(s) for each analyte. The reliability of the model is dependent on the quality of these input data, but since the number of eluents suitable for suppressed IC of anions is quite limited, the acid dissociation constants can be stored in a database within the optimisation software. On the other hand the number of analytes that can be separated using suppressed IC is quite large and the requirement for acid dissociation constants for analytes may impose a restriction on the applicability of some models.

4.3. Summary of the performance of the retention models

Figs. 1 and 2, and Table 4 provide information on which the performance of the retention models can be assessed. Several trends are evident and can be compared with trends noted earlier for non-suppressed IC [1].

1. The linear solvent strength model was the worst performed model and gave particularly poor results when applied to analytes with a charge of greater than -1 . The dominant equilibrium approach gave good results for constant carbonate:hydrogencarbonate experiments, but poor results for constant eluent concentration experiments. The effective charge approach reversed this trend. Both gave poor overall performance, in contrast to non-suppressed IC, where only the dominant equilibrium approach gave noticeably poor results.
2. The remaining models gave excellent performance for singly charged analytes, but only reasonable performance for analytes of higher charge. The exception was the empirical end-points model, which showed consistent performance for

all analytes except phosphate, which gave erratic retention behaviour at the eluent pH values used.

3. In general, only positive errors were observed, with the exception of the multiple species eluent/analyte model, which gave negative errors for the analytes with a charge greater than -1 . This agrees with the trend reported for the non-suppressed data when a polymethacrylate stationary phase was used. Since all of the theoretical models consider only electrostatic effects leading to ion-exchange retention, the presence of other retention mechanisms or the occurrence of factors influencing the ion-exchange process will influence the predictive ability of the models.
4. The six theoretical models gave improved accuracy and precision as their complexity increased, as noted also for the non-suppressed data. However, all theoretical models except the two linear solvent strength model approaches gave sufficiently reliable predictions of retention times to serve as the basis of an optimisation procedure. The empirical end-points model also gave reliable predictions of retention times which were generally superior to those of other models. However, this superiority was not as pronounced as noted earlier for non-suppressed IC.

Despite the fact that the suppressed IC system uses a three-component eluent, prediction of retention data using theoretical models proved to be more reliable than for non-suppressed IC. The chief reason for this may be that carbonate eluents operate predominantly by electrostatic effects and are therefore more amenable to theoretical modelling than phthalate eluents which show strong adsorption effects as well as electrostatic effects. Taking into account the factors outlined in Table 5, together with the data on the accuracy and precision of each model discussed earlier, it can be seen that the empirical end-points model offers ease of numerical solution and requires minimal input data while at the same time providing the most reliable prediction of retention times. The only disadvantage of this method is that, with the exception of the multiple species eluent/analyte model, it requires the greatest number of initial experiments when a two-dimensional optimisation is to be performed. A further advantage of the empirical end-points model as a basis for optimi-

sation is that its accuracy can be improved by iteration during the optimisation process [1].

Acknowledgements

Financial support from the Dionex Corporation is gratefully acknowledged.

References

- [1] J.E. Madden, P.R. Haddad, J. Chromatogr. A 829 (1998) 65.
- [2] D.T. Gjerde, G. Schmuckler, J.S. Fritz, J. Chromatogr. 187 (1980) 35.
- [3] P.R. Haddad, C.E. Cowie, J. Chromatogr. 303 (1984) 321.
- [4] M.J. van Os, J. Slanina, C.L. de Ligny, W.E. Hammers, J. Agterdenbos, Anal. Chim. Acta 144 (1982) 73.
- [5] P.R. Haddad, P.E. Jackson, Ion Chromatography – Principles and Applications, Elsevier, Amsterdam, 1990, Ch. 5.
- [6] D.R. Jenke, G.K. Pagenkopf, Anal. Chem. 56 (1984) 85.
- [7] D.R. Jenke, G.K. Pagenkopf, Anal. Chem. 56 (1984) 88.
- [8] D.R. Jenke, Anal. Chem. 56 (1984) 2674.
- [9] T.B. Hoover, Sep. Sci. Technol. 17 (1982) 295–305.
- [10] M. Maruo, N. Hirayama, T. Kuwamoto, J. Chromatogr. 481 (1989) 315–322.
- [11] D.R. Jenke, Anal. Chem. 66 (1994) 4466–4470.
- [12] P. Hajós, O. Horváth, V. Denke, Anal. Chem. 67 (1995) 434–441.